Y. H. Hu and E. Ruckenstein / Adv. Catal. 48 (2004) 297 345

# Catalytic Conversion of Methane to Synthesis Gas by Partial Oxidation and $CO_2$ Reforming

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The preparation of synthesis gas from natural gas, which is the most important step in the gas to liquid transformation, has attracted increasing attention in the last decade. Steam reforming, partial oxidation, and $CO_2$ reforming are the three major processes that can be employed to prepare synthesis gas. Because steam reforming was reviewed recently in this series [Adv. Catal. 47 (2002) 65], this chapter deals only with the latter two processes.

ADVANCES IN CATALYSIS, VOLUME 48
ISSN: 0360-0564 DOI 10.1016/S0360-0564(04)48004-3

The history of the development of methane conversion to synthesis gas is summarized as an introduction to the partial oxidation of methane, which is reviewed with emphasis on hot spots in reactors, major developments in the reduction of $O_2$ separation costs, and reaction mechanisms. The various catalysts employed in $CO_2$ reforming are examined, with emphasis on inhibition of carbon deposition. © 2004 Elsevier Inc.

## Abbreviations

| | |
|---|---|
| DRIFT | diffuse reflectance infrared Fourier transform |
| EDS | energy dispersive X ray spectrometer |
| FTIR | Fourier transform infrared |
| GHSV | gas hourly space velocity |
| MIEC | mixed ionic/electronic conductors |
| MS | mass spectrometer |
| *R* | reaction rate |
| SPARG | sulfur passivated reforming |
| TEM | transmission electron microscopy |
| TG/DTG | thermal gravimetric/differential thermal gravimetric |
| TPD | temperature programmed decomposition |
| TPH | temperature programmed hydrogenation |
| TPO | temperature programmed oxidation |
| TPR | temperature programmed reduction |
| TPSR | temperature programmed surface reaction |
| WHSV | weight hourly space velocity |
| XRD | X ray diffraction |
| w/o | water in oil |
| XPS | X ray photoelectron spectroscopy |

## I. Introduction

In the 1930s, Standard Oil of New Jersey (*1*) was the first company to employ on a commercial scale the indirect conversion of methane, the main component of natural gas, *via* steam reforming to give synthesis gas, which is a mixture of $H_2$ and CO, with the $H_2$/CO ratio depending on the reactant composition. $CO_2$ is also formed in synthesis gas production, and sulfur compounds are present as impurities. Synthesis gas can be used as a feedstock for numerous chemicals and fuels and as a source of pure hydrogen or carbon monoxide.

The steam reforming process is widely employed today (2). The reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2, \qquad \Delta H^0_{298} \quad 206\ \text{kJ mol}^{\ 1} \tag{1}$$

is expensive because of its endothermic nature, the requirement for low space velocities, and the high $H_2$/CO ratio (3/1), which is unsuitable for synthesis of methanol or the long-chain hydrocarbons made in the Fischer Tropsch process.

The other two main processes for conversion of methane into synthesis gas are partial oxidation and $CO_2$ reforming. In the 1940s, Prettre *et al.* (*3*) first reported the formation of synthesis gas by the catalytic partial oxidation of $CH_4$

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \qquad \Delta H^0_{298} \quad 36\ \mathrm{kJ\ mol}^{\ \ 1} \tag{2}$$

They used a Ni-containing catalyst. In contrast to steam reforming of methane, methane partial oxidation is exothermic. However, the partial oxidation requires pure oxygen, which is produced in expensive air separation units that are responsible for up to 40% of the cost of a synthesis gas plant (*2*) (in contrast, the steam reforming process does not require pure oxygen). Therefore, the catalytic partial oxidation of methane did not attract much interest for nearly half a century, and steam reforming of methane remained the main commercial process for synthesis gas manufacture.

$CO_2$ reforming,

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \qquad \Delta H^0_{298} \quad 247\ \mathrm{kJ\ mol}^{\ \ 1} \tag{3}$$

was investigated as early as 1888 (*4*). Although this process, like steam reforming, is also endothermic, it produces synthesis gas with a lower $H_2/CO$ ratio than steam reforming, and is, therefore, suitable for the Fischer Tropsch synthesis of long-chain hydrocarbons (*5*). Furthermore, it can be carried out with natural gas from fields containing large amounts of $CO_2$, without the pre-separation of $CO_2$ from the feed. Because $CO_2$ is a greenhouse gas that causes warming of the earth and climate change, there are incentives for reducing its concentration in the atmosphere (*6*). $CO_2$ reforming of methane may provide a practical method for consumption of the two greenhouse gases $CH_4$ and $CO_2$. Unfortunately, no industrial technology for $CO_2$ reforming of methane has yet been developed, because no effective, economic catalysts have been discovered (*7*); furthermore, high energy costs may be another drawback preventing commercialization.

When the conventional Ni-containing catalyst for steam reforming was used for $CO_2$ reforming, carbon deposits formed on the catalyst, which deactivated rapidly, at least in the absence of steam. A high molar ratio of $CO_2$ to $CH_4$ ($\geq 3$) could be used to reduce the carbon deposition by inhibiting CO disproportionation, but the selectivity to synthesis gas was found to become much lower than that for the stoichiometric $CO_2$ reforming ($CO_2/CH_4$ 1, molar). Therefore, the inhibition of carbon deposition without extra cost and loss of catalyst performance constitutes a major challenge for $CO_2$ reforming of methane.

In the 1980s, the oxidative coupling of methane to give ethylene and ethane was reported by Keller and Bhasin (*8*), whose discovery prompted numerous attempts to convert methane directly and not only to ethylene and ethane (*8*), but also to methanol and formaldehyde (*9*) (Table I). Research on oxidative coupling of methane was motivated by results showing that the methane was

TABLE I

*Gibbs free energy change, $\Delta G^0$, for methane transformation reactions (10)*

| Reaction | $\Delta G^0$ (kcal mol$^{-1}$) | | | |
|---|---|---|---|---|
| | 400 K | 600 K | 800 K | 1000 K |
| $CH_4 + \frac{1}{2}O_2 \rightarrow \frac{1}{2}C_2H_4 + H_2O$ | −34.6 | −35.1 | −35.8 | −36.4 |
| $CH_4 + \frac{1}{4}O_2 \rightarrow \frac{1}{2}C_2H_6 + \frac{1}{2}H_2O$ | −18.4 | −17.1 | −15.8 | −14.5 |
| $CH_4 + \frac{1}{2}O_2 \rightarrow CH_3OH$ | −25.4 | −23.0 | −20.5 | −18.0 |
| $CH_4 + O_2 \rightarrow HCHO + H_2O$ | −69.0 | −70.0 | −70.8 | −71.2 |
| $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ | −191.3 | −191.3 | −191.3 | −191.3 |
| $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ | −25.0 | −33.9 | −43.1 | −52.5 |
| $CH_4 + H_2O \rightarrow CO + 3H_2$ | 28.6 | 17.3 | 5.5 | −6.5 |

converted into hydrocarbons with higher boiling points, which can be more economically transported than methane; the transportation issue is important because substantial reserves of methane are located in remote places.

The reported results show that Li/MgO, with or without promoters, is the best known catalyst (*11*). However, Pasquon (*12*) reported that the best result obtained in long-run tests has been a $C_{2+}$ yield of only 15% for methane conversions of 15–40%, at 1270–1370 K and a pressure of 1–2 bar, when a 5–10 $CH_4/O_2$ molar ratio was used. In the early 1990s, a consensus emerged that it would be very difficult to achieve a significantly better result than that mentioned above for the oxidative coupling to become an economical industrial process. The reason is that the formation of $CO_2$, rather than of more desirable products (ethylene, ethane, methanol, and formaldehyde), is favored thermodynamically (Table I) when the reactions of methane and oxygen become fast enough to be of practical interest (typically at temperatures exceeding 973 K).

Consequently, in the early 1990s, interest in the direct processes decreased markedly, and the emphasis in research on $CH_4$ conversion returned to the indirect processes giving synthesis gas (*13*). In 1990, Ashcroft *et al.* (*13*) reported some effective noble metal catalysts for the reaction; about 90% conversion of methane and more than 90% selectivity to CO and $H_2$ were achieved with a lanthanide ruthenium oxide catalyst ($L_2Ru_2O_7$, where L = Pr, Eu, Gd, Dy, Yb or Lu) at a temperature of about 1048 K, atmospheric pressure, and a GHSV of $4 \times 10^4$ mL (mL catalyst)$^{-1}$ h$^{-1}$. This space velocity is much higher than that employed by Prettre *et al.* (*3*). Schmidt *et al.* (*14–16*) and Choudhary *et al.* (*17*) used even higher space velocities (with reactor residence times close to $10^{-3}$ s).

An advantage of the high space velocities is the relatively low mass-transfer resistances associated with them.

The catalytic partial oxidation of methane to CO is exothermic, and even a low conversion to $CO_2$ generates a large amount of heat, which leads to significant temperature gradients (hot spots) in the reactor; the temperature may vary by several hundred kelvin over a distance of only 1 mm from the hot spot. Because the partial oxidation is a fast reaction, it is difficult to remove the heat from the reactor as fast as it is generated, particularly from a large-scale reactor. As a result, the process is potentially hazardous and can lead to explosions. The partial oxidation process requires a pure oxygen feed and, therefore, a unit to prepare oxygen by air separation. Therefore, one of the major research goals for making the catalytic partial oxidation a commercial reality is to reduce the cost of the air separation.

The reaction pathways for the partial oxidation reaction are still debated. According to one interpretation, $CO_2$ and $H_2O$ are the primary products, and CO is formed by the reaction of $CO_2$ or $H_2O$ with $CH_4$; according to another interpretation, CO is produced directly by the reaction of $CH_4$ with $O_2$.

In summary, major challenges in the partial oxidation of methane are: (1) designs to avoid excessive thermal gradients (hot spots) in the catalyst bed; (2) reduction of the cost of $O_2$ separation; and (3) elucidation of the reaction pathways as a step toward improved catalyst design.

The purpose of this chapter is to provide a critical assessment of the literature regarding the partial oxidation of methane and the $CO_2$ reforming of methane, with emphasis on the following challenging areas: hot spots, $O_2$ separation cost, and the issues of reaction pathways and catalyst selection; we also address the issue of carbon deposition in the $CO_2$ reforming of methane. The reason why we review these two reactions together is that they have many common characteristics, including the catalysts, the products, and $CH_4$ as reactant.

## II. Partial Oxidation of Methane

### II.A. Hot Spots in Catalyst Beds

In the early 1990s, several papers (*17–20*) reported that one can reach CO and $H_2$ concentrations in excess of those expected at thermodynamic equilibrium by operating the $CH_4$ oxidation reaction at exceptionally high space velocities (GHSV 52,000 mL (g catalyst)$^{-1}$ h$^{-1}$) in a fixed-bed reactor. The following catalysts were employed: $Ni/Yb_2O_3$ (*18*), Co/rare earth oxide (*19*), Co/MgO (*20*), and $Ni/Al_2O_3$ (*17*). However, the actual reaction temperatures (*21*) could have been much higher than those reported (*17–20*). By using an optical pyrometer, Lunsford *et al.* (*22*) found that, during the catalytic oxidation of methane to CO and $H_2$, the combination of a high space velocity, an exothermic reaction, and an active catalyst (Ni/$Yb_2O_3$) gave rise to steep temperature gradients (hot spots). Furthermore, the temperature of the hot spot was greater by as much as 573 K than the temperature measured with a thermocouple located at a distance of only 1 mm from the hot spot in the catalyst bed. If a temperature lower than that of the hot spot is used to calculate the equilibrium concentrations of $CH_4$, CO, $CO_2$, and $H_2$, one can draw the conclusion that the concentrations of CO and $H_2$ exceeded their thermodynamic equilibrium values. However, if the true maximum (hot spot) temperature is used in the calculation, the observed concentrations are found to be somewhat less than those predicted at equilibrium. Indeed, using a careful temperature measurement method, in which a thermocouple end contacted just the top surface of the catalyst bed, Hu *et al.* *(23,24)* found that the $CH_4$ conversion in the presence of Ni/$Al_2O_3$ catalyst was less than that predicted by thermodynamic equilibrium. Furthermore, Hu and Ruckenstein *(25)* observed hot layers (thinner than 1 mm) in NiO/MgO solid solution catalysts and in NiO/$Al_2O_3$ and NiO/$SiO_2$ catalysts during the partial oxidation of methane in a fixed-bed reactor. The hottest layers were located at the top of the bed of the NiO/MgO and NiO/$Al_2O_3$ catalysts, but they were observed to move down and then up for the NiO/$SiO_2$ catalyst bed. The down-and-up movement resulted in an oscillatory temperature of the NiO/$SiO_2$ catalyst at a given position in the bed (Fig. 1), which was absent when the catalyst was NiO/MgO or NiO/$Al_2O_3$ (Fig. 2).

The different temperature behaviors of the three catalysts were attributed to the different strengths of the interactions between the metal oxide and the support. Temperature-programmed reduction (TPR) experiments with 4% $H_2$ in argon indicated that the initial reduction temperature was about 330°C for 13.6 wt% NiO/$SiO_2$, which is near that of pure NiO (about 300°C) *(26)*. In contrast, for 13.6 wt% NiO/$Al_2O_3$ the initial reduction temperature was high (670°C) and no marked reduction peak could be detected even at 800°C for 13.6 wt% NiO/MgO. These results clearly indicate that there are weak interactions between NiO and $SiO_2$ and much stronger interactions between NiO and $Al_2O_3$ and between NiO and MgO.

The weak interactions in Ni/$SiO_2$ might have been responsible for the temperature oscillation by allowing a facile redox behavior of the active nickel sites, namely, the oxidation of $Ni^0$ to NiO by $O_2$ and the reduction of NiO to $Ni^0$ by $CH_4$. The strong interactions characteristic of NiO/$Al_2O_3$ and NiO/MgO were inferred *(25,26)* to inhibit in part the redox behavior of the nickel sites. In the case of NiO/$SiO_2$, according to this interpretation, the freshly reduced NiO located at the inlet of the bed became highly active, causing a hot layer to be generated. The high temperature of this hot layer resulted in sintering of the nickel particles, which led to the loss of activity. Therefore, the reaction is inferred to have taken

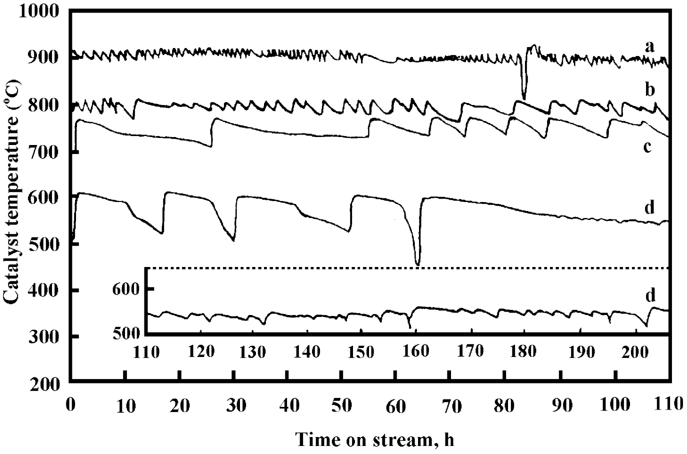

FIG. 1. Relationship between catalyst temperature and reaction time in methane partial oxidation catalyzed by Ni/$SiO_2$ (temperature of the gas phase: (a) 1019 K, (b) 899 K, (c) 809 K, (d) 625 K). The reaction was carried out in a fixed bed reactor (a quartz tube of 2 mm inside diameter) at atmospheric pressure. Before reaction, the feed gas was allowed to flow through the catalyst undergoing heating of the reactor from room temperature to 1073 K at a rate of 25 K min $^{1}$ to ignite the reaction, and then the reactant gas temperature was decreased to the selected value. Reaction conditions: pressure, 1 atm; catalyst mass, 0.04 g; feed gas molar ratio, $CH_4/O_2 = 2/1$; GHSV, 90,000 mL (g catalyst) $^{1}$ h $^{1}$) (25).

place in the neighboring section of the catalyst. As a result, a hot layer propagated downward in the reactor. However, the sintered nickel particles were re-dispersed on the $SiO_2$ support when they were reoxidized by $O_2$, because the oxygen concentration is high when the reaction of $CH_4$ with $O_2$ does not take place. After a certain time, the reoxidized layer near the entrance was again reduced by $CH_4$ and became active again, resulting in a hot layer. The following part of reoxidized nickel on $SiO_2$ can be reduced rapidly by $H_2$ and CO generated near the entrance of the reactor. The redox of the Ni/$SiO_2$ catalyst constitutes a cycle of deactivation and reactivation in each part of the catalyst. The hot layer moved downward in the bed during the time required for the reduction of the entrance layer. Consequently, the time scale of the oscillations was determined by the time scale of the reduction oxidation process.

Recently, such a temperature oscillation was also observed by Zhang *et al.* (27,28) with nickel foils. Furthermore, Basile *et al.* (29) used IR thermography to monitor the surface temperature of the nickel foil during the methane partial oxidation reaction by following its changes with the residence time and reactant concentration. Their results demonstrate that the surface temperature profile was strongly dependent on the catalyst composition and the tendency of nickel to be oxidized. Simulations of the kinetics (30) indicated that the effective thermal conductivity of the catalyst bed influences the hot-spot temperature.

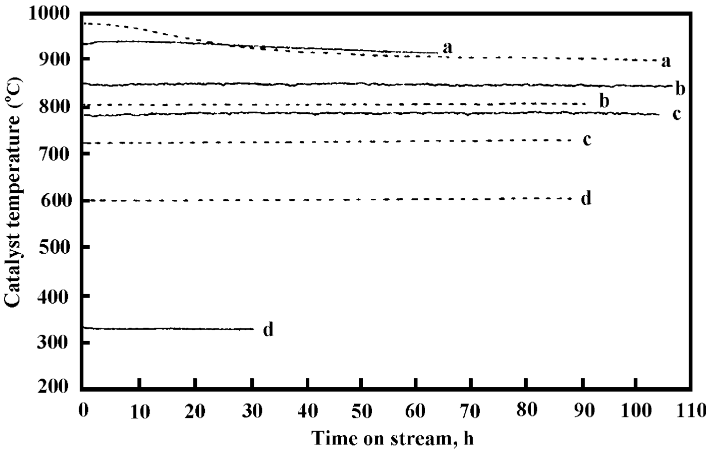

FIG. 2. Relationship between catalyst temperature and reaction time for reaction catalyzed by Ni/$Al_2O_3$( ) and Ni MgO solid solutions ( ); temperature (K) of the gas phase: (a) 1019; (b) 899: (c) 809; (d) 625. The reaction was carried out in a fixed bed reactor (a quartz tube of 2 mm inside diameter) at atmospheric pressure. Before reaction, the feed gas was allowed to flow through the catalyst undergoing heating of the reactor from room temperature to 1073 K at a rate of 25 K min $^{1}$ to ignite the reaction, and then the reactant gas temperature was decreased to the selected value. Reaction conditions: pressure, 1 atm; catalyst mass, 0.04 g; feed gas molar ratio, $CH_4/O_2 = 2/1$; GHSV, 90,000 mL (g catalyst) $^{1}$ h $^{1}$) (25).

Researchers have attempted to minimize thermal gradients, for example, by using fluidized-bed reactors (31 33). Olsbye *et al.* (31) investigated methane partial oxidation in a fixed bed and in a fluidized-bed reactor with a 1.5 wt% Ni/$Al_2O_3$ catalyst operated at 973 K, with a feed flow rate of about 400 (STP) mL min $^{1}$ ($CH_4/O_2/N_2/H_2O$ 2/1/2/0.5, molar) and a catalyst volume of 17 mL. They observed that the maximum temperature difference was only 282 K in the fluidized bed, but 423 K in the fixed bed, indicating that the fluidized-bed reactor is a good heat exchanger because of the rapid mixing of the fluid and the catalyst.

Another way to minimize the temperature gradient (34 40) is to combine the exothermic partial oxidation with an endothermic reaction. Ioannides and Verykios (34) developed a novel reactor consisting of a ceramic tube with metal catalyst films deposited on the inner and outer surfaces. The $CH_4/O_2$ feed enters into the tube, and a large fraction of the heat generated by the methane combustion reactor is transferred through the tube wall towards the outer catalyst film, where an endothermic reforming reaction takes place. With this design, the temperature in the combustion zone is controlled and the hot spots are significantly reduced in magnitude.

Coupling of the endothermic $CO_2$ reforming of methane with the exothermic catalytic partial oxidation of methane can, in addition to overcoming the hazard of overheating, also provide a control of the $H_2/CO$ ratio and thus the selectivity for various Fischer–Tropsch synthesis products. Aschcroft *et al.* (35) carried out this combination of reactions with an $Ir/Al_2O_3$ catalyst, obtaining synthesis gas yields of up to 90% (Table II). However, they found that when nickel-containing catalysts were used, carbon deposits were formed rapidly, except when an excess of $CO_2$ was used. Choudhary *et al.* (41,42) reported that a NiO–CaO catalyst for 15 h exhibited a conversion >95%, with 100% CO selectivity and >90% $H_2$ selectivity, without catalyst deactivation caused by carbon deposition. Furthermore, Ruckenstein and Hu (37) found that the reduced NiO/MgO catalyst provided a high activity and selectivity, as well as excellent stability in the combination process, even when no excess of $CO_2$ was used. They carried out the combined reaction catalyzed by each of the following: a NiO/MgO solid solution, $NiO/Al_2O_3$, and $NiO/SiO_2$. A $CH_4$ conversion of about 90% and selectivities to CO and $H_2$ of about 98% were achieved at 1063 K and a GHSV of 90,000 mL (g catalyst)$^{-1}$ h$^{-1}$ ($O_2/CO_2/CH_4$ = 14.5/26.9/58.6) when a reduced NiO/MgO solid-solution catalyst was used. Almost no change in activity or selectivity occurred during 50 h of reaction. Compared with the reduced NiO/MgO, the reduced $NiO/SiO_2$ and $NiO/Al_2O_3$ catalysts provided lower activities and stabilities. Furthermore, Ruckenstein and Hu (37) observed a decrease in the $CH_4$ conversion with increasing space velocity, whereas during the partial oxidation alone, because of the hot spots, it would have increased (43). This observation implies that the coupling can, indeed, control the thermal behavior of

TABLE II

*Results of catalytic reactions with mixtures of $CH_4$, $O_2$, and $CO_2$ of different compositions in the presence of 1 wt% $Ir/Al_2O_3$ at 1050 K (35)*

| Feed composition (mol%) | | | $CH_4$ converted (%) | $CO_2$ converted (%) | $H_2$ yield (%) | CO yield (%) |
|---|---|---|---|---|---|---|
| $CH_4$ | $CO_2$ | $O_2$ | | | | |
| 64.4 | 3.5 | 32.1 | 92 | 9 | 89 | 86 |
| 59.4 | 20.0 | 20.6 | 87 | 83 | 81 | 86 |
| 58.3 | 23.7 | 18.0 | 84 | 83 | 81 | 84 |
| 58.0 | 28.0 | 14.0 | 83 | 90 | 79 | 85 |
| 49.8 | 48.8 | 1.4 | 91 | 87 | 91 | 89 |

Total gas hourly space velocity, $2 \times 10^4$ mL (mL catalyst)$^{-1}$ h$^{-1}$; pressure, 1 atm. In all the cases, the oxygen conversions were >99.7%.

the reactor. Ruckenstein and Wang (39) found that the Co/MgO solid solution is also an effective catalyst for the combined reaction.

Steam reforming of methane, which like $CO_2$ reforming is endothermic, has also been combined with the exothermic partial oxidation of methane (44 47). This combination process is usually called "autothermal reforming", because no heat addition is required for the reforming reaction. For example, ExxonMobil (44 46, 48 50) extended its experience with fluidized-bed catalytic cracking to the synthesis gas production, developing a process in which the steam reforming was combined with partial oxidation of the natural gas in a single fluidized-bed reactor.

## II.B. Minimizing $O_2$ Purification Costs

Although the partial oxidation of methane with air as the oxidant would at first seem to be a potential alternative to the steam-reforming process, the downstream processing requirements in the conventional process do not tolerate nitrogen (because the cost of compression of synthesis gas diluted by nitrogen to pressures $>$20 atm, which is necessary for downstream industrial processes, is high), and, therefore, pure oxygen must be used. An important advance in the direction of making air a feedstock resulted from the use of an inorganic membrane reactor (51 75). The reactor consists of a dense ceramic membrane (made from mixtures of ionic and electronic conductors, such as $SrFeCo_{0.5}O_x$ (51)) that is permeable only to oxygen; application of this reactor can, in principle, reduce the entire synthesis gas process to a single step, allowing elimination of the oxygen plant and decreasing the total cost of the synthesis gas production by 25 40%. For this reason, this inorganic membrane process has attracted significant commercial interest.

Solid electrolytes are materials that exhibit high ionic conductivities (76). If a solid electrolyte is a pure ionic conductor, the transference number for ions is two or more orders of magnitude greater than that for electrons. Yttria-stabilized zirconia, a pure ionic conductor, is the classical solid electrolyte for solid-state transport of oxygen. However, a system based on a classical solid electrolyte for ionic oxygen transport requires electrodes to transfer the electrons to the reduction interface from the oxidation interface (Fig. 3a). In contrast, the perovskites of the $ABO_3$ type (with the $CaTiO_3$ structure) with dopants in the A and/or B sites, called mixed ionic/electronic conductors (MIEC), provide high conductivities for both oxygen ions and electrons (54 62) (Fig. 3b). The MIEC membrane can be used for the $O_2$ separation without electrodes. The driving force for the overall oxygen transport is the gradient of the oxygen partial pressure across the membrane (77). The dissociation and ionization of oxygen to generate oxygen ions, by capturing the electrons provided by accessible surface electronic states, occur at the oxide surface at the high-pressure feedside. The flux of oxygen ions and the reverse flux

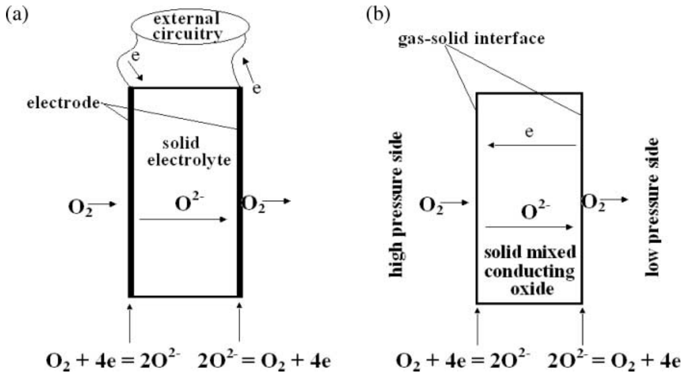

FIG. 3. Oxygen transport in solids. $O_2$ is dissociated and ionized at the reduction interface to give $O^{2-}$ ions, which are transferred across the solid to the oxidation interface, at which they lose the electrons to return back to $O_2$ molecules that are released to the stream. (a) In the solid electrolyte cell based on a classical solid electrolyte, the ionic oxygen transport requires electrodes and external circuitry to transfer the electrons from the oxidation interface to the reduction interface; (b) in the mixed conducting oxide membrane, the ionic oxygen transport does not require electrodes and external circuitry to transfer the electrons to the reduction interface from the oxidation interface, because the mixed conductor oxide provides high conductivities for both oxygen ions and electrons.

of electronic charge carriers across the MIEC membrane constitute a charge-compensation process. The individual oxygen ions from the high-pressure feedside separate from their electrons and recombine again, at the low-pressure permeateside, to form $O_2$ molecules that are released into the permeate stream. Therefore, because of its ability to conduct both oxygen ions and electrons, the MIEC membrane can operate without electrodes attached to the oxide surface and without external circuitry.

Extensive research has been carried out with the acceptor-doped perovskite oxides with the generic formula $La_{1-x}A_xCo_{1-y}B_yO_{3-\delta}$ (where A = Sr, Ba, or Ca and B = Fe, Cu, or Ni) (*77*). Teraoka *et al.* (*54,55,63*) were the first to report very high oxygen fluxes through the cobalt-rich perovskites that can become highly oxygen anion defective at elevated temperatures and reduced oxygen partial pressures. The oxygen-ion conductivity in these perovskites can be 1–2 orders of magnitude greater than those of stabilized zirconias at elevated temperatures, although in the usual ranges of temperature and oxygen partial pressure, the electronic conduction of the perovskite remains predominant (*78,79*).

In the early 1990s, Balachandran *et al.* (*51,64,65*) of the Argonne National Laboratory, in collaboration with Amoco (now part of BP), investigated the partial oxidation of methane using membrane materials consisting of Sr–Fe–Co–O mixed oxides with the perovskite structure, which have high oxygen permeabilities. In their experiments (*51,66*), the membrane tubes, which were

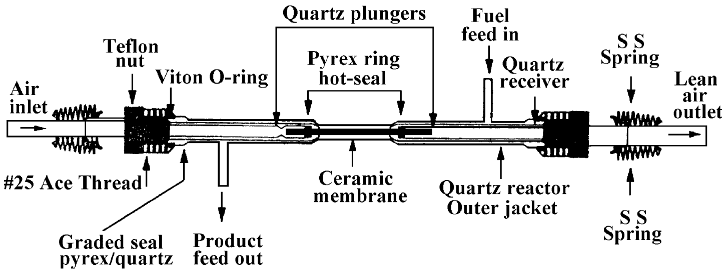

Fig. 4. Configuration of a ceramic membrane reactor for partial oxidation of methane. The membrane tube, with an outside diameter of about 6.5 mm and a length of up to about 30 cm and a wall thickness of 0.25 1.20 mm, was prepared from an electronic/ionic conductor powder (Sr Fe Co O) by a plastic extrusion technique. The quartz reactor supports the ceramic membrane tube through hot Pyrex seals. A Rh containing reforming catalyst was located adjacent to the tube (*51*).

prepared from an electronic/ionic conductor powder (Sr Fe Co O) by a plastic extrusion technique, were investigated for their performance in the quartz reactor sketched in Fig. 4. The quartz reactor supports the ceramic membrane tube with hot Pyrex seals. A Rh-containing reforming catalyst was located adjacent to the tube. In this reactor, air could be used directly, because the membrane itself carried out the separation of oxygen from air. The electrons of the membrane combine with the oxygen from air to generate oxygen anions. The ions migrate through the membrane, from the air side to the methane side. At the methane side, the electrons are stripped from the ions, which are thus converted into oxygen atoms that combine with methane to form the synthesis gas. The freed electrons migrate back to the air side of the membrane, generating fresh oxygen anions, and so on. The experimental results show that the performance of the membrane was strongly dependent on the composition of the material. The most promising material had the composition $SrFeCo_{0.5}O_x$. This membrane operated in a partial oxidation reactor for more than 1000 h at 1123 K (Fig. 5), whereas other mixed-oxide membranes fractured rapidly. A methane conversion of 98% with a 90% CO selectivity was thus achieved. Another advantage of the membrane reactor is that the process does not involve the handling of potentially explosive $CH_4/O_2$ mixtures.

Other early contributions to the membrane processes for partial oxidation of methane include the following: (a) the $La_{0.2}Sr_{0.8}Fe_{0.8}Cr_{0.2}O_x$ membrane of Standard Oil Company at Ohio (now part of BPAmoco) (*67*), which remained stable for more than 1000 operating hours at 1373 K, and (b) a brownmillerite membrane with the general composition $A_2B_2O_5$ (where A and B were not disclosed), consisting of a layer of $BO_6$ octahedra sharing vertices with a layer of $BO_4$ tetrahedra (*68*), which was tested for more than 3000 operating hours at 1173 K and 1 atm with a CO selectivity $>96\%$ and a $CH_4$ conversion $>80\%$. A group at Worcester Polytechnic Institute (*69*) also investigated the partial

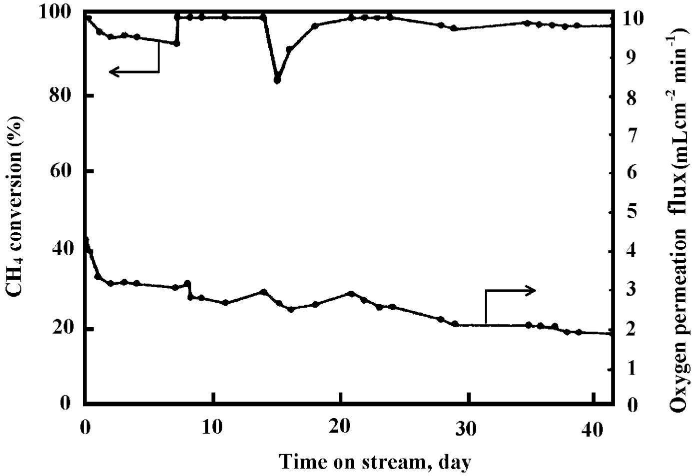

Fig. 5. Methane conversion and oxygen flux during partial oxidation of methane in a ceramic membrane reactor. Reaction conditions: pressure, 1 atm; temperature, 1173 K, feed gas molar ratio, $CH_4$/Ar = 80/20; feed flow rate, 20 mL min$^{-1}$ (NTP); catalyst mass, 1.5 g; membrane surface area, 8.4 cm$^2$ *(51)*.

oxidation of methane to give synthesis gas using a mixed-conducting $La_{(1-x)}A_xFe_{0.8}Co_{0.2}O_{3-\delta}$ perovskite dense membrane reactor at 1123 K, in which the oxygen was separated from air and simultaneously fed into the methane stream. The steady-state oxygen permeation rates for membranes in non-reacting air/helium experiments were in the sequence $La_{0.2}Ba_{0.8}Fe_{0.8}Co_{0.2}O_{3-\delta} > La_{0.4}Ba_{0.6}Fe_{0.8}Co_{0.2}O_{3-\delta} > La_{0.4}Ca_{0.6}Fe_{0.8}Co_{0.2}O_{3-\delta} > La_{0.4}Sr_{0.6}Fe_{0.8}Co_{0.2}O_{3-\delta}$. By packing a 5% Ni/$Al_2O_3$ catalyst directly on the reaction-side surface of the membrane, the researchers obtained a fivefold increase in $O_2$ permeation and a fourfold increase in $CH_4$ conversion. The oxygen, which was continuously transported from the air side, appeared to stabilize the membrane interior, and the reactor could be operated for up to 850 h *(69,70)*.

Recently, Li *et al.* *(71)* demonstrated a promising application of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane for oxygen separation characterized by a high permeation flux (1.1 mL cm$^{-2}$ min$^{-1}$ at 1123 K) and stability (leak-free during partial oxidation). A membrane reactor, prepared from a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane (Fig. 6), was applied successfully to the partial oxidation of methane (with $LiLaNiO_x/\gamma$-$Al_2O_3$ containing 10 wt% Ni as catalyst, located on the top of the membrane) at 1148 K for about 500 h without failure, with a methane conversion >97% and a CO selectivity >95% (Fig. 7) *(72)*. A novel dense catalytic membrane reactor, prepared from the stable conducting perovskite $BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$ and the catalyst LiLaNiO/$\gamma$-$Al_2O_3$ also

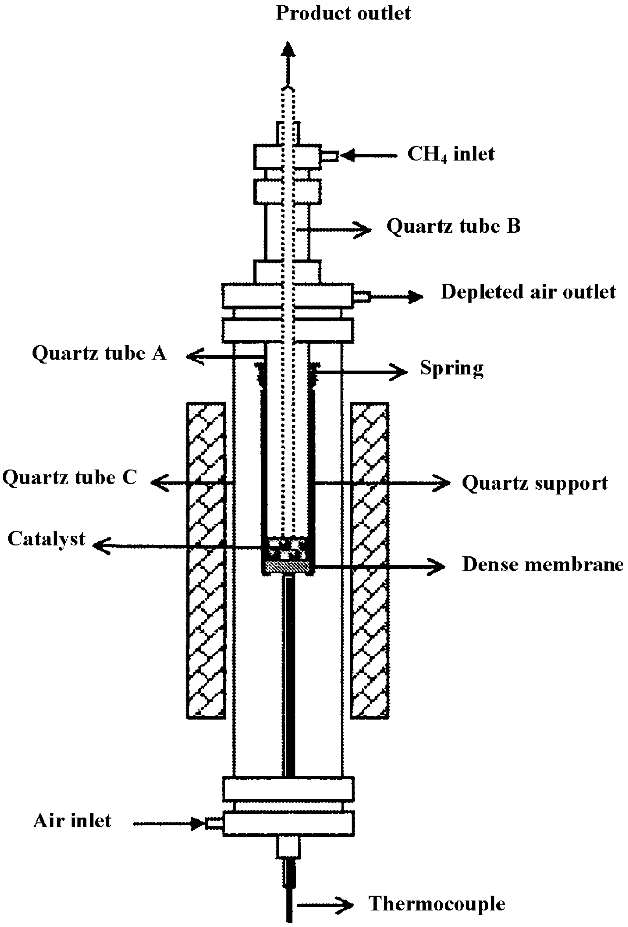

FIG. 6. Configuration of a ceramic membrane reactor for partial oxidation of methane. The membrane disk was prepared by pressing $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3}$ $_{\delta}$ oxide powder in a stainless steel module (17 mm inside diameter) under a pressure of (1.3  1.9) × $10^9$ Pa. The effective area of the membrane disk exposed to the feed gas ($CH_4$) was 1.0 $cm^2$ (*72*).

demonstrated excellent performance for partial oxidation (*73*). This membrane reactor was characterized by a short induction period (2 h), high $CH_4$ conversion (98%) and CO selectivity (about 99%), and excellent stability (more than 2200 operating hours) at 1123 K.

Since 1997, to accelerate the membrane technology towards commercialization, two major alliances have been formed, one comprising Amoco (now part of BP), Praxair, Statoil, Sasol, and Philips, and the other (a US Department of Energy

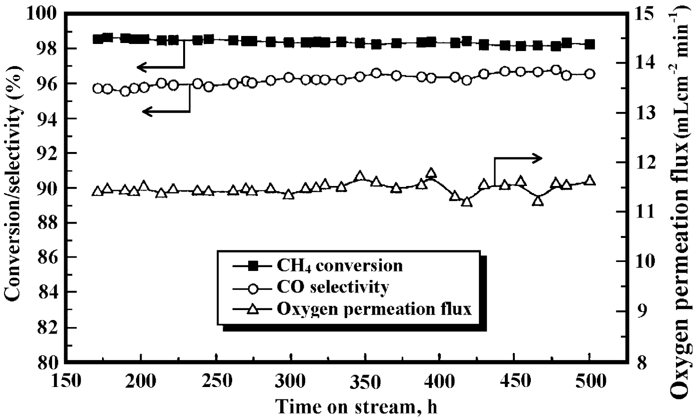

FIG. 7. Methane conversion, CO selectivity, and oxygen flux through the ceramic membrane during the partial oxidation of methane in a ceramic membrane reactor (see Fig. 6). Reaction conditions: temperature, 1148 K; catalyst, 300 mg of LiLaNiO$_x$/γ Al$_2$O$_3$; air flow rate, 300 mL min$^{-1}$ (NTP); feed gas molar ratio, CH$_4$/He = 1/1; feed flow rate, 42.8 mL min$^{-1}$ (NTP) (72).

cost-shared project) made up of Air Products, Arco (now part of BP), Argonne National Laboratory, Babcock and Wilcox, Ceramate (Salt Lake City), Chevron-Texaco, Eltron Research, Norsk Hydro, Pacific Northwest National Laboratory, Pennsylvania State University, and the University of Pennsylvania (*74*).

Notwithstanding the extensive research, there are still hurdles to overcome (*80 82*). Although the mixed conducting membranes offer high oxygen fluxes, they are mechanically and chemically less stable than the traditional stabilized zirconias. Furthermore, the integration of a ceramic membrane into large-scale production units will be difficult, because the ceramics break easily and are not easily manufactured without microscopic voids and fractures. It is also difficult to connect them to other, more flexible materials such as steel pipes. These critical issues represent major challenges to the commercialization of MIEC membrane reactors for the partial oxidation of methane.

Therefore, a team, led by the University of Alaska-Fairbanks, was formed to study these practical issues (*75*), including the composition of the ceramic membrane, seals that would join the ceramic and metal materials, membrane performance, and development of a ceramic that would resist warping and fracturing at the high temperatures of the conversion process.

Another way to eliminate the oxygen plant is to react a metal oxide with methane to yield the synthesis gas in a fluidized-bed reactor (*83 86*). Experiments have shown that copper oxide readily oxidizes methane to carbon monoxide and hydrogen with high selectivity at a temperature of about 1200 K and that the reduced CuO can be reoxidized with air. Lewis *et al.* (*83 86*) proposed a process using two interconnected fluidized beds  a reactor for the hydrocarbon oxidation by the metal oxides (Step 1) and a regenerator for the reoxidation of the reduced metal oxide by air (Step 2). The major advantage of this process is that air can be used directly without pre-separation. A high conversion of about 95% and a selectivity of 90% were thus achieved (*83  86*). However, metal oxide sintering during the reduction  oxidation cycles could be a difficulty.

## II.C. CATALYSTS

In the 1940s, Prettre *et al.* (*3*) reported the formation of synthesis gas *via* the catalytic partial oxidation of $CH_4$ catalyzed by a 10 wt% refractory supported nickel, at temperatures between 973 and 1173 K. Thermodynamic equilibrium corresponding to the catalyst bed exit temperature was achieved under all conditions investigated. In 1970, Huszar *et al.* (*87*) examined the effect of diffusion on methane partial oxidation catalyzed by a single grain of Ni/mullite catalyst in the temperature range of 1033  1173 K and examined the ignition and extinction characteristics of this catalyst. They observed that the nickel catalyst deactivated in an oxidative environment but could recover on reduction. In 1984, Gavalas *et al.* (*88*) investigated the effects of the calcination temperature, pre-reduction, and feed ratio on the reaction of $CH_4/O_2$ mixtures catalyzed by NiO/$\alpha$-$Al_2O_3$ at 843  1033 K. However, under their experimental conditions, the main products were $CO_2$ and $H_2O$.

Since 1990, researchers (*89  148*) have continued to examine nickel-containing catalysts for the partial oxidation of methane, and they also started to use noble metals as catalysts. In 1990, Ashcroft *et al.* (*13*) reported a methane conversion of about 90% and more than 90% selectivity to CO and $H_2$ at 1043 K, atmospheric pressure, and at the high GHSV of $4 \times 10^4$ mL (mL catalyst) $^{1}$ h $^{1}$ for a reaction catalyzed by lanthanide ruthenium oxides, such as $Pr_2Ru_2O_7$, $Eu_2Ru_2O_7$, $Gd_2Ru_2O_7$, $Dy_2Ru_2O_7$, or $Lu_2Ru_2O_7$. In 1992, Hickman and Schmidt (*14*) used platinum monoliths to achieve high selectivities to CO and $H_2$ in the partial oxidation of methane. In the following 10 years, various noble metal catalysts have been examined (Table III) (*89  106*). Compared with the non-noble metal catalysts, the noble metals exhibit high stability with excellent activities and selectivities. The major drawback of the noble metal catalysts is their high cost, which restricts their potential use in industrial processes.

Non-noble metal catalysts, particularly those containing nickel, have also been investigated extensively since 1990. Lunsford *et al.* (*107*) examined a 25 wt% $Ni/Al_2O_3$ catalyst in the temperature range 723  1173 K. Carbon monoxide selectivities approaching 95% and virtually complete conversion of the methane were achieved at temperatures above 973 K. The authors observed that, under their operating conditions, the calcined catalyst bed consisted of